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TSDC and DR Studies in PEO Complexed

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by

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TSDC AND DR STUDIES IN PEO COMPLEXED WITH INORGANIC SALTS

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ABSTRACT

TSDC studies have been carried out on PEO complexed with inorganic salts. The results clarify the structure of the DR spectra observed previously for these materials. In the case of the Y relaxation region, which is associated with the amorphous phase, several new relaxations are observed in PEO complexed with the various salts. Changes in the strength of these peaks give rise to the differences observed previously in the DR spectra for these materials, not only between different salts but between different concentrations of the same salt. The results show that in the amorphous phase below the glass transition, at least, the ions occupy very well defined positions vis a vis the polymer chains. Models for the relaxation are discussed along with the influence of the ions.

1. INTRODUCTION

In previous papers [1-5] the dielectric relaxation (DR) spectra for poly(ethylene oxide) (PEO) complexed with various lithium, sodium, potassium, calcium, and barium salts were reported. Interesting differences in relaxation peak position and strength were observed between the various samples. Subsequently, thermally stimulated depolarization current (TSDC, Ionic thermocurrents, ITC) studies were carried out on PEO and PEO complexed with KSCN [6]. Insight into the DR results was obtained. In the present note, TSDC data are reported for PEO complexed with sodium, calcium, and barium salts for which previous DR results have been given. The TSDC data reveal the underlying structure of the DR spectra.

2. EXPERIMENT

The samples were prepared by dissolving PEO (Polysciences, MW 5×10^6) in methanol or acetonitrile at about 60C. In the case of the complexed materials, the salts were added in the correct proportions and dissolved simultaneously. The resulting solutions were poured onto a teflon plate and allowed to dry in air, then vacuum at about 60C for 24 hours. Aluminum electrodes were evaporated onto the resulting films. The films studied in the present work had been stored under desiccant for about two years. No further thermal treatment was applied to the samples prior to measurement and all temperature cycling associated with the TSDC studies were below room temperature. These films were cut to form disks about 8 mm in diameter and 0.7 mm thick.

The TSDC measurements were made using equipment which has been described previously [6,7]. In general, TSDC measurements were made with a polarizing voltage of 300 V, and a linear heating rate of about 7.5K/min was used. Details of individual data runs are given in Table 1. The

sample chamber was usually back-filled with helium gas to improve thermal contact with the samples and the control was generally to within 0.025K from 80K to 300K. Typical results are shown in figs. 1 and 2.

In several cases a peak cleaning technique had to be used to isolate a particular peak. While this is not generally appropriate for processes with a distribution of relaxation parameters, it was done as a compromise to allow a reasonably simple data analysis. Care was taken to ensure that the temperature of maximum current and the curve symmetry were preserved.

3. DATA ANALYSIS

A Gaussian-broadened TSDC equation was fitted to the data. The formalism is that the current density, $J(T,E)$, was taken to be:[8]

$$J(T,E) = \frac{P_o}{\tau_o} \exp\left[-\frac{E}{kT} - \frac{1}{\beta\tau_o} \int_{T_o}^{T} \exp\left(-\frac{E}{kT'} \right) dT' \right] \quad (1)$$

where P_o is the dipole moment per unit volume and β is the heating rate. τ is the preexponential and E is the activation enthalpy in the Arrhenius expression for the relaxation time:

where
$$\tau = \tau_o \exp(E_o/kT). \quad (2)$$

which is assumed. T_o is the starting temperature of the data run and the integral was calculated using Squire's approximation where $x=E/kT'$:[9]

$$\int_{T_o}^{T} \exp\left(-\frac{E}{kT'} \right) dT' = \left. \frac{T'\exp(-x)(x+3.0396)}{(x^2+5.0364x+4.1916)} \right|_{T'=T_o}^{T'=T} \quad (3)$$

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Next, the monoenergetic equation was modified to include the effects of distributed parameters by assuming a distribution function in E:

$$dJ = f(E)J(T,E)dE \tag{4}$$

and defining the distribution function to be a Gaussian:

$$f(E) = \exp\left(-\frac{(E-E_o)^2}{2\,\sigma^2}\right) \tag{5}$$

where E_o is the mean activation energy of the reorientation.

Finally, the limits of integration were set at 0 and $3E_o$ so that the working equation becomes:

$$J(T) = \int_0^{3E_o} f(E)J(T,E)dE \; . \tag{6}$$

The fitting was done by manual adjustment of E_o, τ_o, σ, and a peak height factor. The "best fit" criterion was visual rather than mathematical. The reason for this was that this procedure was the most efficient and accurate way of excluding the spurious contributions from space charge or peak cleaning residuals which were always present. A typical data set and "best fit" curve are shown in fig. 4.

4. DISCUSSION

4.1 Dielectric Relaxation

As has been well established [1-5], dielectric relaxation spectra for uncomplexed PEO at 100 Hz show relaxation peaks at about 160 K (Y peak), 223 K (α_a peak associated with the glass transition) and a high

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temperature peak in the region of 250 K (α_c peak) which is largely masked by the DC conductivity. When the PEO is complexed with inorganic salts, this basic composition is preserved but the positions, strengths and shapes of the peaks vary [1,2,5].

Specifically, PEO complexed with calcium thiocyanate shows the α_c peak at about 250 K and the Y peak at 140 K, i.e. the Y peak occurs at a lower temperature than in the uncomplexed material. PEO complexed with barium thiocyanate shows the α_c peak also at about 250 K, but the Y peak is at about 180 K, that is, at a higher temperature than the Y peak in the uncomplexed material. In both these cases, despite the fact that the DC conductivity is lower than in the case of the uncomplexed PEO, the α_a peak is not observed. Presumably, this is due to the fact that the glass transition temperature is shifted to about 35°C and 55°C for $Ca(SCN)_2$ and $Ba(SCN)_2$ complexed PEO, respectively [5]. Consequently, the α_a relaxation, if it exists, is hidden beneath the DC conductivity.

In the case of sodium thiocyanate and sodium perchlorate complexed materials, only the Y peak is observable. For these materials, the DC conductivity is high and thus, the α_a and α_c relaxations, if they exist, are masked by the DC conductivity. The Y peak in NaSCN complexed PEO looks very similar to that in the uncomplexed PEO [1], but PEO: $NaClO_4$ appears to have a Y peak which is a little broader and shifted to slightly higher temperatures, and for $PEO_8:NaClO_4$ the Y peak is skewed to higher temperatures, especially at lower concentrations [2].

4.2 Thermally Stimulated Depolarization Currents

As shown previously [6] the TSDC spectrum for uncomplexed PEO shows

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the γ relaxation at about 118 K and the α_c relaxation at 170 K. The evidence for this identification is, of course, that the fitting parameters obtained from the TSDC equation can be used to predict the position of the DR peak via the usual expression $\omega\tau = 1$ where τ is given by eq. (2). Calculations using the data in Table 1 of ref. 6 verify the equivalency.

To complete the discussion of the relationship between DR and TSDC results, it was found that all the materials showed a high temperature peak which was attributed to space charge effects. That peak was discussed

for uncomplexed PEO in ref. 6 and for all the present materials, the highest temperature peak listed in Table 1 is attributed to space charge (sc). That peak then is associated with the free ions in the material and is the TSDC equivalent of ionic conductivity. Those peaks will not be considered further in the present report.

The first important feature of the TSDC studies is that all complexed materials exhibit a peak at about 118 K as does the uncomplexed PEO and thus it is associated with the γ peak. This is not surprising as none of the materials are fully complexed as the stoichiometry for crystalline complexed material is on the order of 3:1 or 4:1 [10] and thus a signal from uncomplexed PEO might be expected. However, the 118 K peak is rather strong in the complexed materials and thus it may be that the same charge configuration responsible for the γ relaxation in uncomplexed PEO may be present in the complexed material. For example, the polar groups responsible for the γ relaxation midway between ions may not be strongly affected by their presence. Some support for this is that the α_c relaxation is not observed in PEO complexed with either NaSCN or $NaClO_4$. A further study of different concentrations will

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be interesting to resolve this question.

Next, as seen in fig. 1, both the $Ca(SCN)_2$ and the $Ba(SCN)_2$ complexed materials show a peak centered at about 172 K, which is designated the α_c peak on the basis of the previous DR studies [5]. In this case, it is likely that some of the peak, at least, is due to the presence of uncomplexed PEO which is obvious from the DSC thermograms [5].

However, the most interesting result is that the TSDC results show the reason for the difference between the DR spectra for $PEO:Ba(SCN)_2$ and $PEO:Ca(SCN)_2$ both from each other and from uncomplexed PEO, as is apparent from figs. 2 and 3. The reason is obvious from inspection of fig. 1. Specifically, TSDC enables the detection of a peak on the low temperature side of the γ peak for $PEO:Ca(SCN)_2$ while the $PEO:Ba(SCN)_2$ has a peak on the high temperature side. Specifically, when the $PEO:Ca(SCN)_2$ sample is polarized at 92 K a new peak is revealed with a maximum current at 103 K. In contrast, when the $PEO:Ba(SCN)_2$ sample is polarized at 125 K and peak cleaned to 115 K, data fitting indicates a peak centered at about 134 K. Thus the apparent shift of the γ peak noted in the DR results is in reality the result of the growth of different peaks in addition to the same γ peak observed in the uncomplexed PEO.

Similarly, in the case of sodium thiocyanate and sodium perchlorate, TSDC also reveals distinct peaks which explain the DR results. For the PEO:NaSCN samples, the normal γ peak is dominant, but additional peaks are observed both above and below γ in temperature. In particular, peak cleaning at 141 K after polarization at 145 K reveals a peak at 156 K.

It is interesting that this peak has approximately the same activation energy and preexponential as the Y_3 peak observed in PEO:KSCN. The peak at lower temperatures, (T_m at 104 K for polarization at 95 K) is much weaker than the other two, and does not appear to correspond to any of the peaks previously observed in PEO complexed with KSCN. Thus it is fortuitous that the DR Y peak remains in approximately the same position as for uncomplexed PEO.

A similar situation exists for $PEO_{4.5}:NaClO_4$ in that the normal Y peak is observed at about 118 K, but the dominant peak in this case is one at about 156 K for polarization at 145 K and cleaning at 141 K. Again, as seen in Table 1, this peak has an activation energy and preexponential factor which are very close to those reported previously for the Y_3 peak in PEO:KSCN. It is clear from fig. 2 that the amount by which the Y_3 peak dominates the spectrum is a function of concentration. An increase in the relative strength of the higher temperature peaks in the lower concentration material is observed using the same experimental parameters. This same shift in peak strength gives rise to the skewed peak seen in the DR results for $PEO_8:NaClO_4$.

4.3. Microscopic interpretation

In two extensive review articles [11,12], Boyd describes the evidence that the Y relaxation is associated with the amorphous phase. Thus, the present results concerning the Y relaxation impact ion motion since it is well known that ionic conductivity takes place in the amorphous phase [13-16]. Although it is clear that the relaxation is due to relatively simple conformational motions, the nature of the charge

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configuration associated with the Y relaxation is not well understood. Boyd goes on to discuss the various models for the Y relaxation, including "three-bond," "five-bond," and "kink" motions.

However, it is clear that these motions do not control ionic conductivity, at least at high temperatures, as it is well known that large scale segmental motions control the ionic conductivity [13-17]. Rather, the results concerning the Y relaxation are important as they reflect the structure of the polymer. Specifically, it is clear that the presence of ions in PEO produces a small number of well defined relaxations, some of which are common to different complexing ions. Consequently, it is concluded that the ions take on a well defined distribution in the glassy phase. The presence of the ions can lead to relaxations with both higher and lower activation enthalpies than for the Y relaxation. On the basis of the "kink" inversion model, for example, for the case of ions far from the kink, one would expect that much of the Y relaxation would be preserved while for ions in the vicinity of the kink, the potential barrier will be changed depending upon the ion or ions involved. It may be, for example, that it is energetically favorable for the anions or cations to selectively occupy sites at well defined distances from the kink, in which case well defined relaxations would result. Theoretical modelling is clearly called for.

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REFERENCES

1. J. J. Fontanella, M. C. Wintersgill, J. P. Calame, and C. G. Andeen, Solid State Ionics, 8, 333 (1983).

2. M. C. Wintersgill, J. J. Fontanella, J. P. Calame, D. R. Figueroa, and C. G. Andeen, Solid State Ionics, 11, 151 (1983).

3. M. C. Wintersgill, J. J. Fontanella, P. J. Welcher, and C. G. Andeen, J. Appl. Phys., 58, 2875 (1985).

4. J. J. Fontanella, M. C. Wintersgill, P. J. Welcher, J. P. Calame, and C. G. Andeen, IEEE Trans. EI, EI-20, 943 (1985).

5. J. J. Fontanella, M. C. Wintersgill, J. P. Calame, and C. G. Andeen, J. Polymer Sci.: Polymer Phys., 23, 113 (1985).

6. M. C. Wintersgill, J. J. Fontanella, P. J. Welcher, and C. G. Andeen, J. Appl. Phys., 58, 2811 (1985).

7. C. Andeen, G. E. Matthews, Jr., M. K. Smith, and J. Fontanella, Phys. Rev., B19, 5293 (1979).

8. C. Bucci and R. Fieschi, Phys. Rev. Letters, 12, 16 (1964).

9. R. Squire, J. Comp. Phys., 6, 371 (1970).

10. T. Hibma, Solid St. Ionics, 9&10, 1101 (1983).

11. R. H. Boyd, Polymer, 26, 323 (1985).

12. R. H. Boyd, Polymer, 26, 1123 (1985).

13. M. B. Armand, J. M. Chabagno and M. J. Duclot, in Fast Ion Transport in Solids, J. N. Mundy and G. K. Shenoy, Eds., Pergamon Press, New York, 1979, p. 131.

14. A. Killis, J. F. LeNest, A. Gandini, H. Cheradame, and J. P. Cohen-Addad, Solid St. Ionics, 14, 231 (1984).

15. C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno and

P. Rigaud, Solid State Ionics, 11, 91 (1983).

16. J. J. Fontanella, M. C. Wintersgill, M. K. Smith, J. Semancik, and C. G. Andeen, J. Appl. Phys., 60, 2665 (1985).

17. S. G. Greenbaum, Y. S. Pak, M. C. Wintersgill, J. J. Fontanella, J. W. Schultz, and C. G. Andeen, J. Electrochem. Soc., to be published.

TABLE 1. Activation parameters and identification of various ITC peaks. T_c is the peak cleaning temperature.

Identification	$\beta(K/s)$	$T_p(K)$	$T_c(K)$	$T_m(K)$	$E(eV)$	$\sigma(eV)$	τ_o $(10^{-14}s)$	P_o/τ_o $(10^{16}A/m^2s)$
$PEO_{4.5}NaSCN$								
-	0.130	86	no	99.1	0.292	0.014	6.8	15
γ_2?	0.129	95	no	104.2	0.305	0.020	8.8	10.8
γ	0.129	110	111	122.0	0.352	0.016	15.0	7.0
γ_3?	0.133	145	141	156.0	0.450	0.017	18.0	6.37
sc	0.129	175	176	185.2	0.519	0.01	49.0	3.6
$PEO_{4.5}NaClO_4$								
-	0.129	83	no	94.6	0.279	0.016	5.5	17.7
-	0.125	98	101	111.3	0.327	0.018	8.0	12.4
γ	0.127	110	98	119.1	0.347	0.025	12.0	7.8
γ_3?	0.128	145	141	156.6	0.447	0.019	29	3.8
sc	0.129	180	177	193.5	0.543	0.02	60	2.0
$PEO_{6.5}Ba(SCN)_2$								
γ	0.125	105	96	115.7	0.335	0.022	11	8.7
-	0.129	125	115	133.7	0.338	0.026	15	6.4
α_c	0.125	163	149	172.9	0.49	0.027	39	2.62
sc	0.127	210	204	223.8	0.629	0.027	70	1.6
$PEO_{6.5}Ca(SCN)_2$								
γ_2?	0.127	92	no	103.2	0.304	0.018	7.0	13.6
γ	0.147	110	98	117.3	0.344	0.027	10.0	9.23
α_c	0.127	163	151	171.8	0.488	0.028	40	2.54
sc	0.130	210	201	225.7	0.634	0.033	71	1.47

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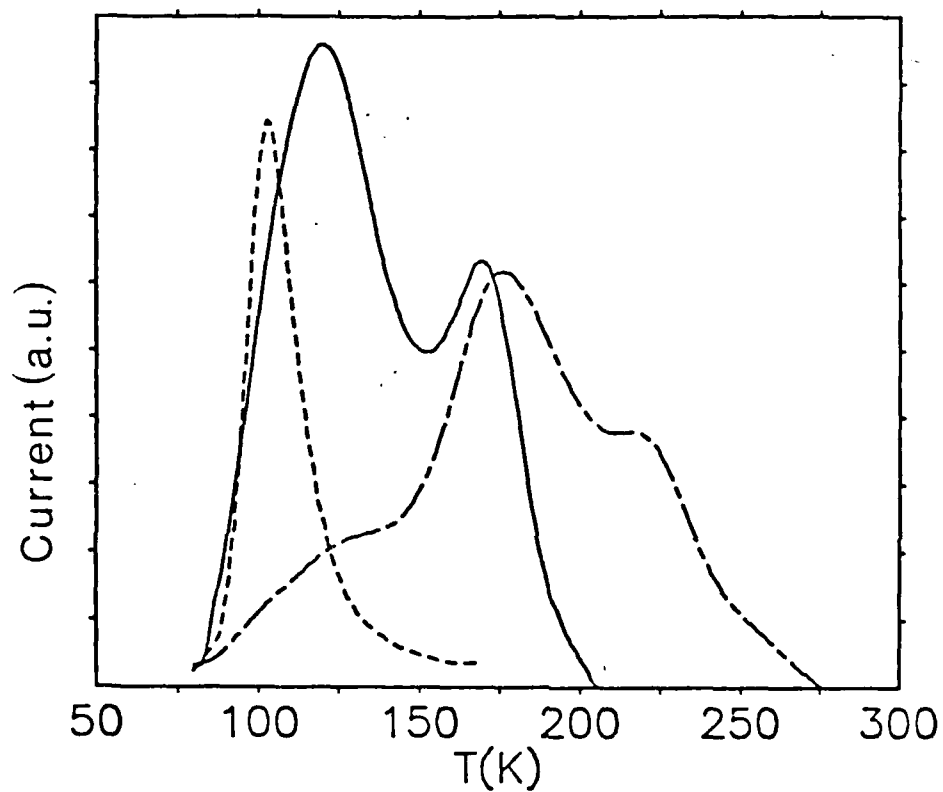
Figure 1. TSDC spectra for: (a) uncomplexed PEO--solid line, (b) $PEO_{6.5}Ba(SCN)_2$--chain link, and (c) $PEO_{6.5}Ca(SCN)_2$--dash. The strength for one material relative to another is not significant.
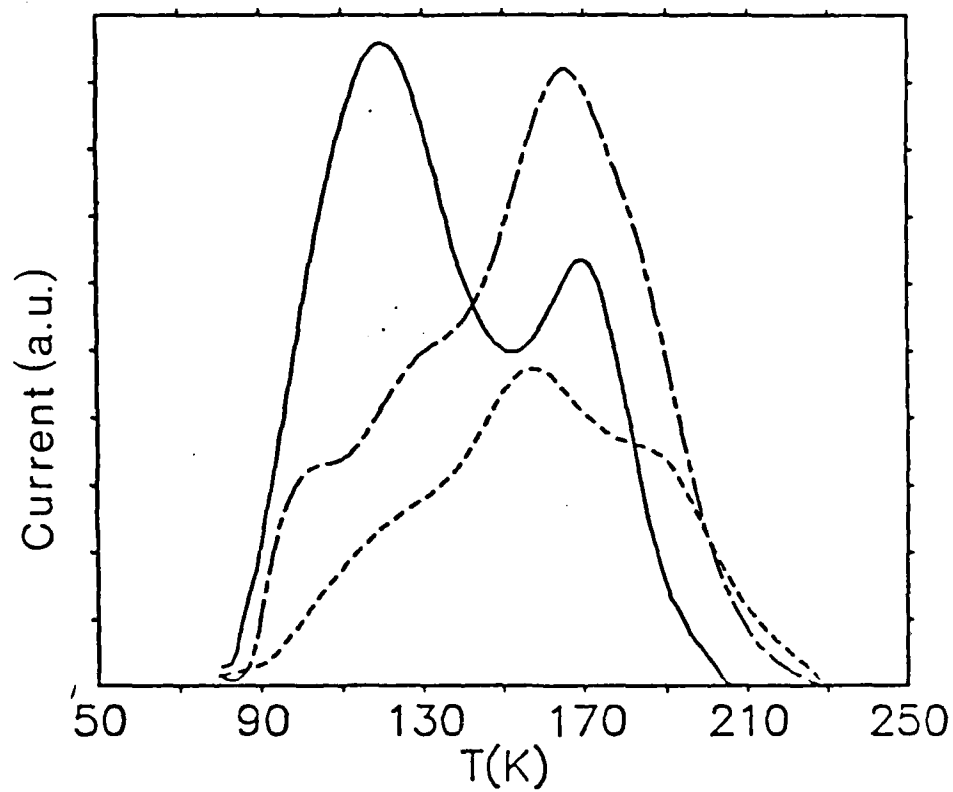
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Figure 2. TSDC spectra for: (a) uncomplexed PEO--solid line, (b) PEO_8NaClO_4--chain link, and (c) $PEO_{4.5}NaClO_4$--dash. The strength for one material relative to another is not significant.
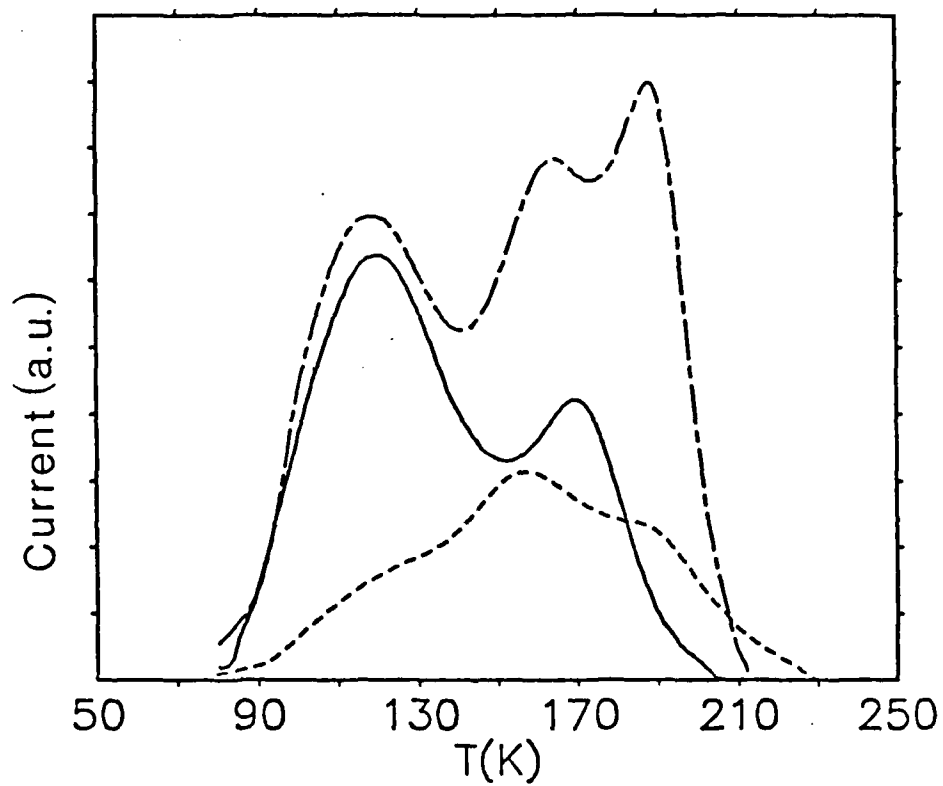
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Figure 3. TSDC spectra for: (a) uncomplexed PEO--solid line, (b)
$PEO_{4.5}NaSCN$--chain link, and (c) $PEO_{4.5}NaClO_4$--dash. The strength for one
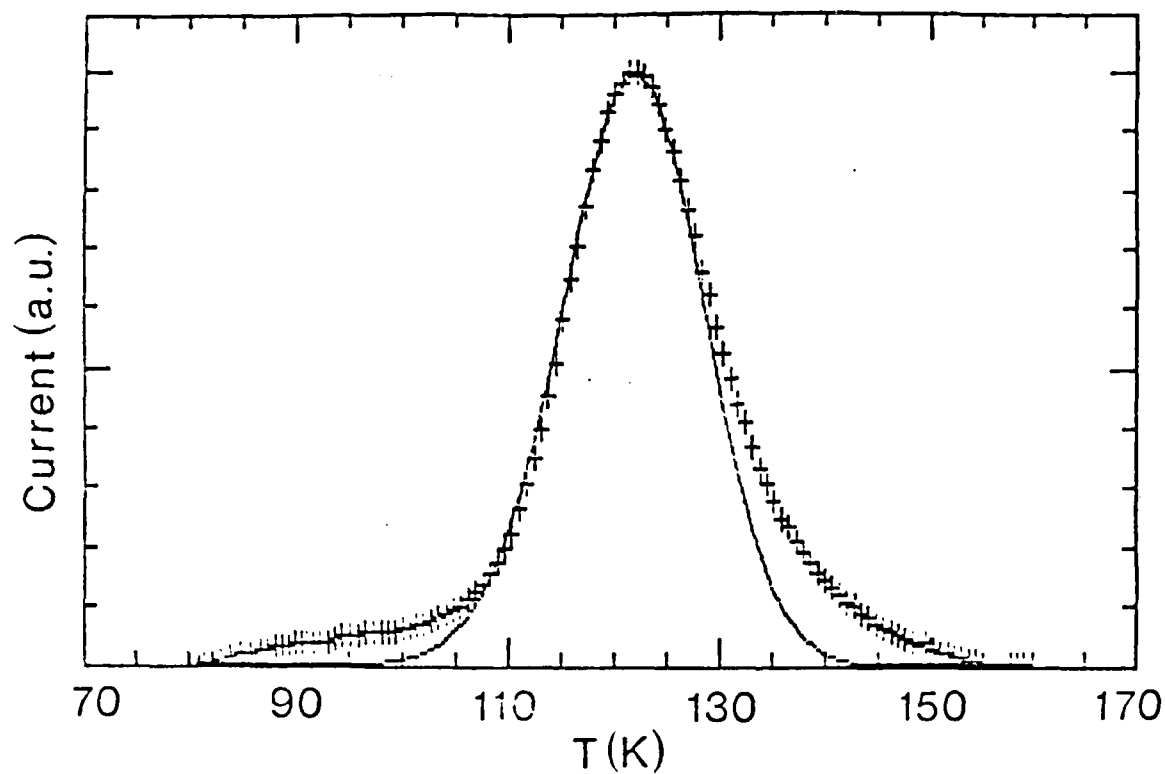material relative to another is not significant.

Figure 4. "Peak-cleaned" TSDC spectrum and "best-fit" curve for the γ
relaxation in $PEO_{4.5}NaSCN$. The material is the same as that for which the
full TSDC spectrum is shown in fig. 3b. The relevant parameters are given
in line 3 of Table 1.

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